

**<sup>193</sup>Ir Mössbauer Study of Chloro(carbonyl)bis-(triphenylphosphine)(buckminsterfullerene)iridium**

A. Vértes,<sup>†</sup> M. Gál,<sup>‡</sup> F. E. Wagner,<sup>§</sup> F. Tuczak,<sup>||</sup> and P. Güttlich<sup>\*,||</sup>

Department of Nuclear Chemistry, Lorand Eötvös University, P.O. Box 32, H-1518 Budapest, Hungary, Department of Inorganic Chemistry, Lorand Eötvös University, H-1518 Budapest, Hungary, Physik-Department E-15, Technische Universität, München, D-85748 Garching, Germany, and Institut für Anorganische und Analytische Chemie, Johannes Gutenberg Universität, D-55099 Mainz, Germany

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At present, the buckminsterfullerenes are one of the most extensively studied research fields in chemistry. The most important member of this group is the icosahedral C<sub>60</sub>, which has 20 six-membered and 12 five-membered rings. The diameter of C<sub>60</sub> is 710 pm, and the C-C bond is 143 pm at the 6-6 ring fusion and 140 pm at the 6-5 ring fusion (there are no 5-5 ring fusions). The isolation of fullerenes in macroscopic quantities<sup>1,2</sup> has resulted in an explosion-like increase of the number of studies dealing with their chemical and physical properties.<sup>3,4</sup> In this paper we have used Mössbauer spectroscopy to obtain information about the nature of the chemical bond between C<sub>60</sub> and the central Ir atom in Vaska's coordination compound chloro(carbonyl)bis-(triphenylphosphine)iridium (CCTI).<sup>5</sup> The CCTI-fullerene complex was described by Balch et al.,<sup>6</sup> and they found that two neighboring carbon atoms of fullerene are bonded to CCTI in a side-on ( $\eta^2$ ) fashion with 219 pm bond lengths and a 41° bond angle. The distance between the two bonded carbon atoms is 153 pm.<sup>6</sup> The other bond lengths in this complex are Ir-P = 238 pm and Ir-Cl = 240 pm; the other bond angles are P-Ir-P = 113.3° and Cl-Ir-C (in carbonyl) = 179.6°. The two triphenylphosphine ligands in *trans*-positions in the square planar Vaska's complex are shifted in a nearly *cis*-geometry upon bonding to C<sub>60</sub>.<sup>6</sup> Thus, the equatorial plane is surrounded by the two phosphorus atoms and by the two carbon atoms of the fullerene and Cl and CO are axially bonded. Since the P-Ir-P bond angle is almost three times larger than that of the C-Ir-C bond, the geometry of the fullerene adduct is strongly distorted octahedral, almost trigonal bipyramidal.

We have measured the Mössbauer spectrum of the adduct of chlorocarbonylbis(triphenylphosphine)iridium (CCTI) with buckminsterfullerene (C<sub>60</sub>) and, for comparison, remeasured the spectra of both the parent compound CCTI and its adduct with tetracyanoethylene, CCTI-TCNE. Mössbauer spectra of the <sup>193</sup>Ir 73 keV  $\gamma$ -transition were taken at 4.2 K. The source was metallic <sup>193</sup>Os, which, being hexagonal, exhibits a quadrupole splitting of about 0.48 mm/s. The individual lines of the quadrupole doublets of the studied samples are therefore not simple Lorentzians; this circumstance is taken into account in the fitting procedure. The full widths at half-maximum of the individual superimposed Lorentzian lines obtained by the least-squares fits are between 0.75 and 0.79 mm s<sup>-1</sup> and thus but slightly larger than the natural line width of 0.60 mm s<sup>-1</sup>. The relevant

Table I

absorber	isomer shift <sup>a</sup> (mm/s)	quadrupole splitting, (mm/s)	ref
IrCl(CO)(PPh <sub>3</sub> ) <sub>2</sub>	+0.05 ± 0.015	7.74 ± 0.03	15
	-0.06	6.66	16
	-0.03	6.54	17
	+0.022 ± 0.010	6.52 ± 0.03	<i>b</i>
IrCl(CO)(PPh <sub>3</sub> ) <sub>2</sub> ( $\eta^2$ -TCNE)	-0.20 ± 0.02	1.83 ± 0.04	11
	-0.194 ± 0.010	1.837 ± 0.015	<i>b</i>
IrCl(CO)(PPh <sub>3</sub> ) <sub>2</sub> ( $\eta^2$ -C <sub>60</sub> )-5C <sub>6</sub> H <sub>6</sub>	-0.259 ± 0.010	2.714 ± 0.015	<i>b</i>

<sup>a</sup> The isomer shifts refer to metallic iridium. <sup>b</sup> Our measurements.

Mössbauer parameters are collected in Table I, and the spectra are displayed in Figure 1. Isomer shifts in this paper are given relative to metallic iridium.

Vaska's complex has been prepared by a standard procedure<sup>7</sup> from iridium(III) trichloride trihydrate, recrystallized triphenylphosphine, and freshly distilled dimethylformamide. The CCTI-TCNE complex is obtained by mixing stoichiometric amounts of Vaska's compound and tetracyanoethylene in benzene under nitrogen.<sup>8</sup> The buckminsterfullerene adduct is synthesized after Balch.<sup>6</sup> The CCTI-C<sub>60</sub> adduct crystallizes with 5 benzene molecules.

In the adducts of CCTI with electron-deficient olefins such as TCNE or buckminsterfullerene the CO stretching frequency  $\nu$ (CO) has been used to monitor the degree of electron withdrawal from the metal to the olefin.<sup>5,6</sup> CCTI itself has a  $\nu$ (CO) value of 1953 cm<sup>-1</sup> which increases upon bonding of an electron-deficient substituent to a higher value reflecting a decreasing ability of the metal to donate electron density into antibonding  $\pi$ -orbitals of CO. As  $\nu$ (CO) is observed at 2057 cm<sup>-1</sup> in CCTI-TCNE and at 2014 cm<sup>-1</sup> in the CCTI-C<sub>60</sub> adduct, it has been concluded that C<sub>60</sub> is a weaker electron acceptor than TCNE.<sup>6</sup> It is of interest to compare this result to our Mössbauer data.

The spectrum of the pure CCTI complex is given in Figure 1a. Formally, the central ion has a charge of +1 (configuration 5d<sup>8</sup>-6s<sup>0</sup>). The large quadrupole splitting (7 mm s<sup>-1</sup>; Table I) reflects a low-spin d<sup>8</sup> configuration (d<sub>x<sup>2</sup>-y<sup>2</sup></sub> empty) typical for square-planar complexes of group VIII metals. The value of the isomer shift, however, is about that of Ir metal whereas typical isomer shifts for octahedral, ionic Ir complexes<sup>9</sup> extrapolated to the d<sup>8</sup>s<sup>0</sup> configuration would give an isomer shift of about -4 mm s<sup>-1</sup>. The large positive shift to the observed value around 0 mm s<sup>-1</sup> must be attributed to a significant population of 6s orbitals which can be rationalized in terms of a hybridization of 5d<sub>x<sup>2</sup>-y<sup>2</sup></sub> with 6s both belonging to the same irreducible representation in the square-planar (*D<sub>4h</sub>*) symmetry of the complex.

The vibrational data mentioned above suggest that the d-electron density which is probed by the CO stretching frequency is reduced in the CCTI adducts as compared to the parent complex. Since the isomer shift goes to higher (less negative) values if the number of d-electrons is reduced (corresponding to a ratio  $\Delta R/R > 0^{10}$ ), the isomer shift in the adducts is expected to move to higher values as compared to CCTI. On the contrary, it is observed that  $\delta$  shifts to more negative values (-0.26 mm/s for CCTI-C<sub>60</sub> and -0.20 mm/s for CCTI-TCNE). This must be due to a decrease in 6s electron density in the adducts which overcompensates the decrease of the shielding effect of the d-electrons due to  $\pi$ -back-bonding. This decrease in 6s electron density is understandable as the adducts have a distorted octahedral symmetry which allows for 5d-6s hybridization to a smaller extent

<sup>†</sup> Department of Nuclear Chemistry, Lorand Eötvös University.

<sup>‡</sup> Department of Inorganic Chemistry, Lorand Eötvös University.

<sup>§</sup> Technische Universität.

<sup>||</sup> Johannes Gutenberg Universität.

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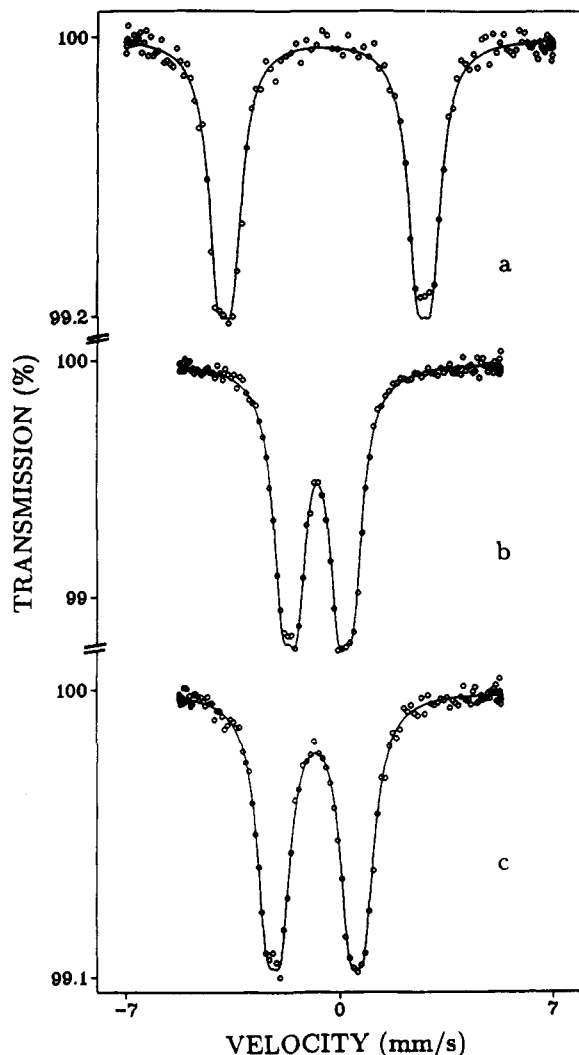


Figure 1.  $^{193}\text{Ir}$  Mössbauer spectra of (a)  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ , (b)  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-TCNE})$ , and (c)  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-C}_{60})$ . The spectra were recorded at 4.2 K, and the source was metallic  $^{193}\text{Os}$ .

than the square-planar configuration of CCTI itself. Nevertheless, the population of 6s must still be appreciable: even if an oxidation state of +3 is attributed to the Ir ion in the CCTI-TCNE adduct as suggested by XPS data,<sup>11</sup> the isomer shift should have a much more negative value if 6s were empty. As regular octahedral symmetry does not allow s-d mixing, we attribute the high value of s-electron density to the strong distortion of the adducts from  $O_h$  symmetry. In addition, bonding of the two "soft" and electron-

rich phosphine ligands in CCTI and its adducts further acts to transfer electron density into the 6s orbital.

The coordination geometries around the Ir ion are very similar in the TCNE and  $\text{C}_{60}$  adducts; i.e., both substituents coordinate in a side-on ( $\eta^2$ ) fashion in *trans* position to the two phosphine ligands.<sup>6,12</sup> Also, the strong electron affinity of the two central atoms in TCNE, due to the effect of four cyano groups, is supposed to be similar to that of the carbon atoms in  $\text{C}_{60}$ .<sup>13</sup> Since both  $\text{C}_{60}$  and TCNE are much weaker  $\sigma$ -donors than the two phosphine ligands, we assume that the Ir s-electron densities are comparable in both adducts and that the difference in isomer shift is attributable to a variation in the d-electron density. As CCTI-TCNE has a slightly less negative ( $-0.20$ ) isomer shift than CCTI- $\text{C}_{60}$  ( $-0.26 \text{ mm s}^{-1}$ ), TCNE is a stronger d-electron acceptor than  $\text{C}_{60}$ . This finding is in line with the result from vibrational data (*vide supra*). Finally, the difference in quadrupole splitting between CCTI-TCNE ( $1.8 \text{ mm s}^{-1}$ ) and CCTI- $\text{C}_{60}$  ( $2.7 \text{ mm s}^{-1}$ ) needs to be considered. Both values are considerably smaller than that of CCTI itself ( $6.5 \text{ mm s}^{-1}$ ; cf. Figure 1), which is understandable as the  $e_g$  orbitals are now roughly equally populated, i.e. formally  $(t_{2g})^6(d_{x^2-y^2})^1(d_{z^2})^1$  as compared to  $(t_{2g})^6(d_{z^2})^2$  in CCTI. Thus, the valence electron contribution to the electric field gradient is expected to be considerably lower in the adducts than in CCTI itself.<sup>14</sup> A drastic decrease of the electric quadrupole splitting has also been observed in  $\text{H}_2$ -adducts of  $(\text{PPh}_3)_3\text{Ir}(\text{CO})\text{X}$  complexes both with  $\text{X} = \text{Cl}$  and for a number of other ligands.<sup>15,18</sup> The actual value of the quadrupole splitting in the adducts, however, is very sensitive to the electronic properties of both the phosphine and the substituents in *trans* position: whereas the phosphine ligands donate electron density into the  $d_{x^2-y^2}$  orbital and therefore act to accumulate electron density in the equatorial plane, the TCNE or  $\text{C}_{60}$  ligands are primarily  $\pi$  acceptors and withdraw electron density from  $d_{x^2-y^2}$ . Empirically, it is found that the quadrupole splitting in the CCTI adducts increases with decreasing  $\pi$  acceptor ability of the  $\eta^2$  substituent;<sup>11</sup> i.e., the smaller the capability of the  $\eta^2$  ligand to act as a  $\pi$  acceptor, the larger the charge buildup in the equatorial plane. The same "push-pull" mechanism can also be formulated with the empty Ir 6p<sub>x</sub> and p<sub>y</sub> orbitals. In both cases, the larger quadrupole splitting of CCTI- $\text{C}_{60}$  as compared to CCTI-TCNE indicates a weaker  $\pi$  acceptor ability of  $\text{C}_{60}$  than of TCNE, in agreement with the result from the variation of the Mössbauer isomer shift and the CO stretching frequency.

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